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A PROPOSAL TO KIDD CREEK DIVISION OF FALCONBRIDGE MINES LTD. FOR THE COMMERCIALIZATION OF THE BIORECOVERY PROCESS FOR SELENIUM

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CONFIDENTIAL

BIORECOVERY OF SELENIUM

Summary

Over the past eighteen months CANMET has developed a biological process for the recovery of elemental selenium from Kidd Creek Mine Smelter & Roaster Weak Acid Effluents.

The weak acid effluents are neutralized with lime to pH 7.0, combined with nutrients for the bacteria, and treated in a rotary biological contactor (RBC). The selenium-laden biomass is recovered from the RBC effluent stream, digested with dilute caustic soda, and the elemental selenium is recovered as a fine powder.

From the laboratory studies to date, >95% of the selenium can be removed from solution, and following biomass digestion, metallic selenium can be recovered having a purity of >95%. Since the digested biomass is recycled to the RBC as nutrient for the process, there is no organic sludge to dispose. A flowsheet of the proposed process has been developed and a patent application for the process is being filed.

Kidd Creek Mines Engineering Group has calculated the capital and operating costs of the process based on the information provided by CANMET and CMS Rotordisk Inc. (supplier of Rotating Biological Contactors) to date.

On an industrial scale, recovery of selenium from 500 gpm effluent containing 40 ppm of selenium would produce gross revenues of $509,000 to $815,024 per year depending on the selling price of the selenium product. It appears that this process can be scaled up to commercial practice with an acceptable level of risk. CANMET is prepared to co-operate with Kidd Creek to further develop and commercialize this process under a licence agreement whereby Kidd Creek would acquire the right to CANMET's proprietary technology.

Introduction

Kidd Creek Mines advised CANMET that they required an economic means of removing selenium from their smelter and roaster weak acid effluents. Preliminary laboratory studies by CANMET indicated that a bioreductive process was feasible for this purpose.

BIORÉCUPÉRATION DU SÉLÉNIUM

Résumé

Depuis 18 mois, le CANMET travaille à l'élaboration d'un procédé biologique permettant de récupérer à l'état élémentaire le sélénium à partir des effluents faiblement acides provenant du four de fusion et de grillage de la mine Kidd Creek.

On neutralise les effluents faiblement acides avec de la chaux jusqu'à un pH de 7,0, en même temps que l'on ajoute des nutriments destinés aux bactéries, puis on les traite dans un contacteur biologique rotatif (CBR). On récupère la biomasse chargée de sélénium dans le courant d'effluent liquide s'échappant du CBR, on la soumet à une digestion en présence de soude caustique diluée et l'on récupère le sélénium élémentaire sous forme de fine poudre.

D'après les études réalisées jusqu'à présent en laboratoire, il est possible d'extraire plus de 95 % du sélénium à partir d'une solution, puis après digestion de la biomasse, on peut extraire du sélénium métallique caractérisé par un degré de pureté supérieur à 95 %. Étant donné que la biomasse digérée est recyclée dans le CBR où elle sert de nutriment pendant le déroulement du procédé, il n'y a plus de boues organiques à rejeter. On a élaboré un schéma de principe du procédé proposé, et l'on cherche actuellement à le faire breveter.

Le Kidd Creek Mines Engineering Group a calculé les coûts en capital et coûts d'exploitation du procédé, à partir de l'information fournie par le CANMET et par la compagnie CMS Rotordisk Inc. (fournisseur des contacteurs biologiques rotatifs) jusqu'à présent.

À l'échelle industrielle, la récupération du sélénium à partir de 500 gpm d'effluent contenant 40 ppm de sélénium produirait des recettes brutes de 509 000 $ à 815 024 $ par an, suivant le prix de vente du produit à base de sélénium. Il semble que l'on puisse appliquer ce procédé à l'échelle commerciale sans risques disproportionnés. Le CANMET est prêt à coopérer avec la compagnie Kidd Creek, pour perfectionner et commercialiser ce procédé aux termes d'un contrat de licence par lequel la compagnie Kidd Creek acquerrait le droit d'utiliser la technologie exclusive du CANMET.

As the effluent volumes will vary from 500 to 1000 gpm, CANMET conducted a preliminary cost estimate on three possible process designs using:

i) rotary biological contactors (RBC's);
ii) continuous stirred tank reactors (CSTR's); and
iii) immobilized cell, fluidized bed reactor.

The preliminary capital cost estimates indicated that an RBC design would be the most economic.

On these findings, CANMET contacted CMS Rotordisk and supported a NRC-IRAP proposal to optimize the process and establish operating parameters.

NRC-IRAP Study

The NRC-IRAP study indicated:

1. Soluble selenium levels in the effluent could be reduced by >95% in a retention time of 4 h with a Se:BOD (biological oxygen demand) ratio of 1:20 at pH 7.0 at 22-23°C.
2. A continuous inoculum of selenite reducing organisms could be supplied by using sewage to effluent (v/v) ratio of 1:10.
3. A suitable method of recovery of the elemental selenium from the biomass was not achieved.

When CMS Rotordisk Inc. was unsuccessful in optimizing the bioreductive process and in recovering the elemental selenium from the biomass, CANMET took over the task.

The CANMET Biotechnology Group tackled the recovery of selenium from the biomass using three different approaches:

i) enzymatic digestion of cell material;
ii) use of surfactants; and
iii) surfactants and enzymes.

These three approaches failed but during one surfactant test at pH 10.0, good cellular breakage and selenium recovery were noted. Caustic soda had

been used to adjust the pH, and an alkaline digestion of the biomass had occurred. Efforts were then concentrated on optimizing the conditions for mild alkaline digestion of the biomass.

Further laboratory studies showed that selenium greater than 95% purity can be recovered. The process development utilized approximately 1.5 person years and results from the cumulative efforts of Mr. Joseph Salley, Dr. W.D. Gould and Dr. R.G.L. McCready. The process needs to be tested on an industrial scale.

Process Concept

The recovery of selenium from the effluent stream is based on the bacterial reduction of selenite by the non-pathogenic Escherichia coli. E. coli are normal flora in the human and animal gastro-intestinal tracts and are non-pathogenic except in special circumstances. The organisms reduce selenite to red amorphous selenium which is deposited within the cells as small granules. Once the cell has accumulated a large number of selenium granules, it dies, falling off the disks of the RBC and is carried in the effluent from the RBC.

The cellular biomass can be recovered from the effluent by solid-liquid separation techniques such as (i) continuous high speed centrifugation; (ii) flocculation and settling; or (iii) tangential flow filtration. The selenium-laden biomass may then be treated by one of two methods for selenium recovery: (a) The biomass may be digested with 0.25 N caustic soda at a solid:liquid ratio of 5 g/L. The soluble organic fraction from this digestion is recycled to the RBC as a carbon source for cellular growth. The metallic selenium is washed extensively with water and recovered as a fine powder. (b) The second option is to extract the selenium from the cells with boiling 1% Na_2SO_3. The boiled extract is then treated with alumina to adsorb the organic cellular components, filtered to remove the organic laden alumina, and the selenium is precipitated by acidification of the filtrate with H_2SO_4. The selenium is washed extensively with water, collected and dried as a fine powder. The organic-laden alumina can be treated with hot caustic soda to remove the organics which are recycled to the RBC as a carbon source and the alumina can be re-used as an organic adsorbant.

Laboratory Results to Date

1. Selenite Concentration Tolerance Tests:
   Shake flask studies have indicated that selenite reduction to amorphous elemental selenium can be achieved over the concentration range of 10 to 500 ppm and selenium as oxidized salts in the effluent.
2. Removal of Selenium From Solution:
   Shake flask studies and RBC laboratory studies consistently show that >95% of the selenium is removed from solution either as elemental selenium or as organo-selenium compounds within the biomass.
3. Recovery of Elemental Selenium From Biomass:

(a) Na_2SO_3 Extraction Method:

As selenium is soluble in hot Na_2SO_3, the biomass was extracted with boiling 1% w/v Na_2SO_3. The biomass residue was removed by filtration, the filtrate cooled and then acidified to re-precipitate the selenium. Using this procedure elemental selenium of 50.6% purity was recovered. FTIR analysis of the sample indicated organic contamination, probably during acid precipitation, as indicated by the Amide I and Amide II peaks in the spectrum (Fig. 1). Two additional S-O peaks are also seen.

A two-step extraction with boiling 1% Na_2SO_3 resulted in recovery of selenium of 93.6% purity. The FTIR spectrum for this sample (Fig. 2) showed a much smaller Amide II peak, with little change in the Amide I peak. The S-O peaks were reduced but still present, thereby reducing the metal purity.

Reverting to the one-step boiling 1% w/v Na_2SO_3 extraction, the solution after boiling was filtered through a column of activated alumina to adsorb the organic cellular components. The filtrate was then acidified with H_2SO_4 to precipitate the selenium; the alumina could be regenerated by extraction with dilute alkali, in which case the alkaline organic solution would be recycled to the RBC as a carbon source. Alternatively, the alumina could be thermally regenerated, but the organics will be lost as CO_2.

(b) Dilute Alkali Digestion:

A sample of biomass was extracted by boiling in 0.25 N NaOH for 30 min. The sample was cooled, placed in a large separatory funnel fitted with a stop-cock and side-arm 1½" above the lower stop-cock. The black, elemental selenium settled in the cone, the soluble protein and 0.25 N NaOH were decanted through the side stop-cock, and the sample was repeatedly washed with distilled water, collected and dried. Chemical and FTIR analysis of this sample indicated a selenium purity of 99.1% with only a trace of organic contamination (Fig. 3). A small Amide I peak was still detectable.

The chemical analysis is presented in Table 1.

Table 1 - Analysis of the Bio-Recovered Selenium

Element	%
Se	99.1
Fe	0.015
Si	0.013
Mg	0.0013
Cu	0.003
Al	<0.002

A barrel of neutralized smelter weak acid effluent was received from Kidd Creek and chemically analyzed (Table 2).

Table 2 - Chemical Analysis of Neutralized Kidd Creek Weak Acid Effluent

Element	ppm
Cu	0.3
Pb	0.4
Zn	270
Se	33.0
Te	<1.0

Seventy litres of this solution was treated in a 30 L capacity CMS Rotordisk RBC. The solution was combined with raw sewage in a 10:1 ratio and dry milk powder was added as a carbon source to increase the BOD to Se ratio to approximately 20:1.

The effluent biomass was recovered by centrifugation at 12,000 rpm using a Sharples High Speed Continuous Flow Centrifuge at a rate of 1 L/min.

The biomass (~30 g wet wt) was extracted (or digested) in 1.5 L of 0.25 N NaOH. This resulted in a very viscous solution which retarded the settling of the selenium granules. For rapid settling of the elemental selenium, the biomass should be digested under the following conditions: 5 g of wet biomass per litre of 0.25 N NaOH.

Although the purity of the selenium was less than that recovered in previous experiments, digestion of 5 g wet biomass per litre of 0.25 N NaOH will result in a product of 99% purity. As seen in Table 3, the amounts of contaminating metals in the product are extremely low, and the organic content can be reduced under the digestion step by controlling the ratio of biomass to volume of caustic soda.

Table 3 - Analysis of the Selenium Produced from Kidd Creek Effluent

Element	%
Se	89.6
Al	0.033
Ca	0.035
Cr	0.010
Cu	0.010
Fe	0.21
Mg	0.006
Ni	0.001
Pb	0.005
Zn	0.005
Organic debris	10.085

The presence of organic components was confirmed by the FTIR spectrum presented in Fig. 4. There are high Amide I and II peaks as compared to Fig. 3.

Full Scale Process

A schematic diagram of the proposed process is presented in Fig. 5. For start-up of the process the selenium containing effluent will have to be neutralized to pH 7.0 with a limestone slurry. Once the caustic digestion of biomass is initiated and the soluble cellular components in the caustic are recycled to the neutralization tank as a carbon source for the organisms, the limestone slurry consumption will be reduced as the recycled caustic will be used for the final pH adjustment.

Assuming a flow rate of 500 gpm, the total volume per day will be 720,000 gal; this volume will require 7 industrial scale RBC's rated at 100,000 gpd capacity. Biomass will be sloughed from the RBC into the RBC effluent, producing a slurry containing 0.4 to 0.5 g of biomass per litre at a flow rate of 500 gpm. The biomass may be recovered by three alternative methods: continuous flow high speed centrifugation, flocculation or by tangential flow filtration. If centrifugation or flocculation are used, a viscous cell paste or a floc will be produced and it will have to be reslurried in 0.25 N caustic soda for digestion. If tangential flow filtration is used, a slurry will be produced having approximately 1/50th the input volume. Thus, it will contain about 20 g wet weight of biomass/L; this will have to be diluted down to 5 g of biomass/L and then sufficient dry caustic soda added to produce a 0.25 N solution. The digestion will require two 60,000 gal tanks. The accumulated biomass over a 12 h period in a volume of ~48,000 gal will be adjusted to 0.25 N with caustic soda and boiled for 30 min.

The boiling dilute caustic will solubilize the biomass material; the solution is cooled and the metallic selenium will be allowed to settle. The organic laden caustic solution will then be recycled to the neutralization step to provide a carbon source for the organisms and for final pH adjustment of the acidic selenium feed solution. The metallic selenium will be reslurried in water, allowed to settle and the supernatant decanted and

discarded. Two subsequent water washes will produce an alkali and organic free product of >99% purity.

The metallic selenium could then be dried in an evaporator, melted and poured as ingots or sprayed into water for pelletization.

Economics

As this process only requires effluent neutralization to pH 7.0 rather than the current technology which requires pH adjustment to >11.0, significant savings will be realized due to the reduced consumption of lime. Secondly, neutralization to a lower pH will produce less metal-laden sludge, thereby reducing handling and disposal costs.

The weak acid smelter effluent typically contains 30-40 ppm of selenium. At a flow rate of 500 gpm, the expected gross revenues from the process are summarized in Table 4.

Table 4 - Potential Gross Revenues from Selenium Recovery

Effluent concentration	$/lb	Gross revenue
30 ppm Se @ 500 gpm	5.00	$382 040
	6.00	458 448
	7.00	534 856
	8.00	611 264
40 ppm Se @ 500 gpm	5.00	509 390
	6.00	611 268
	7.00	713 146
	8.00	815 024

Intellectual Property

The process described in this report for the recovery of selenium from the specified effluents is proprietary to CANMET. There have been no disclosures of the process or process details to other parties. By way of a non-disclosure agreement signed by CANMET and Kidd Creek, all relevant details on this process are being transmitted to Kidd Creek. The proprietary information on this process is being included in drafting up a patent

application, which is to be soon filed in Canada. Extension of this patent coverage to other countries will be subject to the terms of the transfer of CANMET's rights on this invention to Kidd Creek via a licence. Upon review of this document, and a positive response from Kidd Creek, CANMET expects to immediately (perhaps by mid July, 1988 at the latest) commence negotiations with Kidd Creek on the terms of this licence. No rights are granted (or may be assumed by) Kidd Creek until this licence agreement is concluded.

To initiate this licensing process, Kidd Creek will be expected to provide a brief (4-6 pages) Business Plan for exploiting this CANMET invention. That document shall address Kidd Creek's corporate objectives, production and sales targets, process development plan, the level and type of support required from CANMET, and the scheme which Kidd Creek proposes for sharing revenues with CANMET. The document shall also address confidentiality and promotional requirements, and extent of patent coverage that is desired.

Work on this invention was initiated by CANMET exclusive of the IRAP Laboratory Network Project in which CMS/Rotordisk Inc. attempted to demonstrate the feasibility of recovering selenium from Kidd Creek's effluents using biomass in a rotating biological contactor. To reiterate, this process is the exclusive property of Her Majesty in right of Canada, as represented by the Minister of Energy, Mines and Resources, through the Canada Centre for Mineral and Energy Technology.

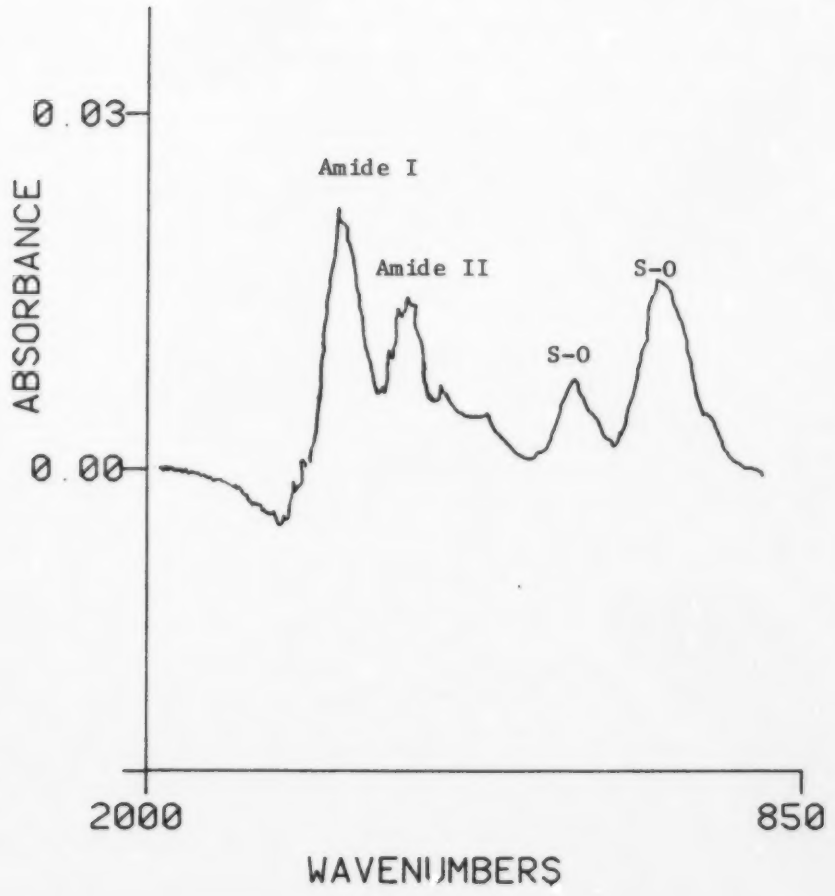

Fig. 1 - FTIR spectrum of selenium extracted with boiling 10% w/v Na_2SO_3 followed by acid precipitation

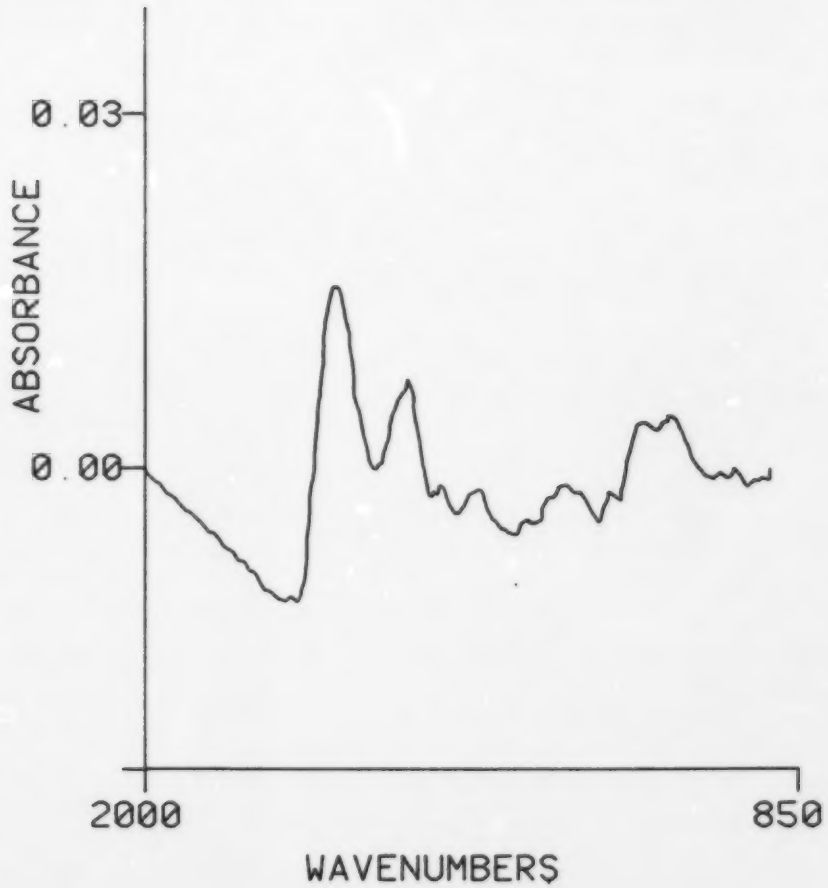

Fig. 2 - FTIR spectrum of selenium extracted in a two step boiling 10% w/v Na_2SO_3 followed by acid precipitation

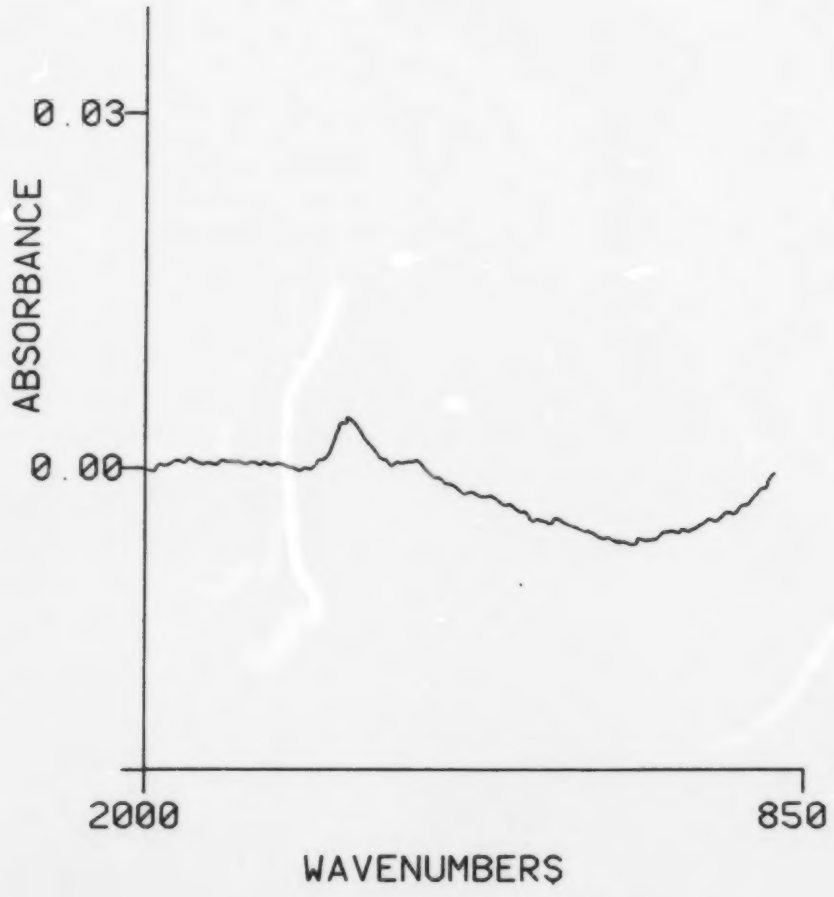

Fig. 3 - FTIR spectrum of selenium extracted with boiling 0.25 N NaOH and 3 water washes

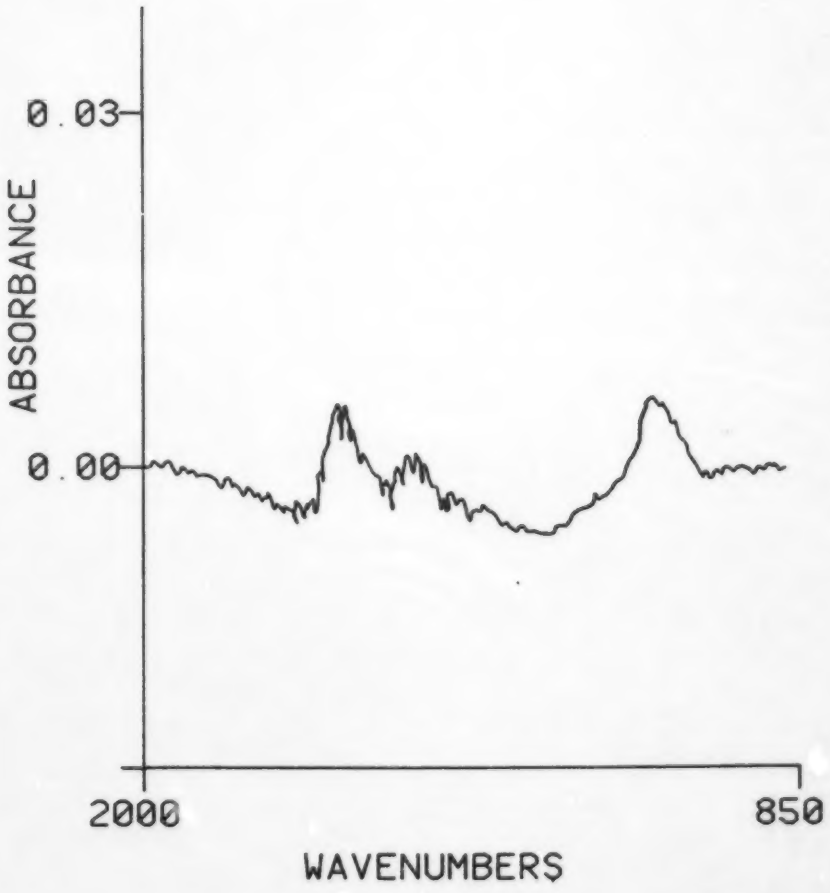

Fig. 4 - FTIR spectrum of selenium recovered from weak acid effluent by bioreduction followed by 0.25 N NaOH extraction

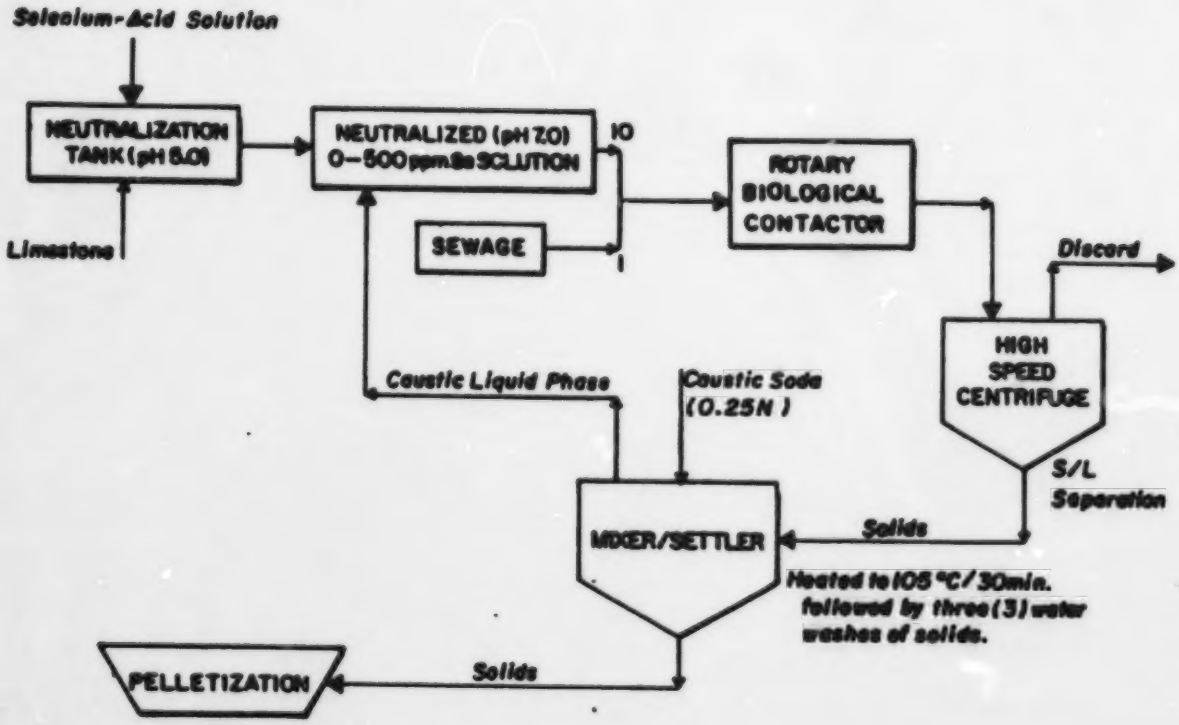

Fig. 5 - Flowsheet of proposed industrial process for selenium recovery from weak acid smelter effluent